

# CHAPTER 3

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## **Weak Acid/Base Systems in Dilute Acidified Lakes and Streams of the Adirondack Region of New York State**

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Aqueous acidification is a serious water quality problem facing many regions of the world today. Acidification of waters in regions underlain by siliceous bedrock may be attributed to the relatively short retention time of waters and relatively slow mineral dissolution kinetics, which limit hydrogen ion neutralization within the soil environment. Such waters are characteristically low in dissolved salts (dilute) and dissolved inorganic carbon (DIC) due to limited contact with the soil environment. However, elevated levels of aqueous aluminum have been observed in dilute acidified waters [1–3]. Because dilute water systems are inherently low in DIC, they are low in inorganic carbon buffering capacity. Consequently other weak acid/base systems, such as aluminum and natural organic acids, may be important in the pH buffering of dilute waters.

Important terms used in evaluating acid/base systems are: base neutralizing capacity (BNC), which is the equivalent sum of all acids that can be titrated with a strong base, and, acid neutralizing capacity (ANC), which is the equivalent sum of all bases that can be titrated with a strong acid. Total BNC and ANC can be considered as the composite of individual acid/base systems.

Several researchers have investigated non-inorganic carbon, weak acid/base systems in dilute waters. Dickson [4] observed that elevated levels of aluminum increased the BNC of Swedish lakes. Waters were strongly buffered by aluminum in the pH range 4.5–5.5. The BNC of aluminum was particularly evident when acidified lakes were treated with base (limed). Aluminum BNC was comparable in magnitude to hydrogen ion and inorganic carbon BNC; therefore, the presence of aluminum substantially increased base dose requirements and the cost associated with the restoration of acidified lakes.

Johannessen [5] investigated nonhydrogen/inorganic carbon buffering in Nor-

wegian waters. While reiterating the importance of aluminum as a buffer in dilute acidified waters, she also evaluated the role of natural organic acids. Natural organic matter reduced the degree to which aluminum hydrolyzed in the pH range 5.0–5.5, presumably due to complexation reactions and therefore decreased the buffering of aluminum. Natural organic matter also participated in proton donor/acceptor reactions; the extent to which total organic carbon (TOC) would dissociate/associate protons was  $7.5 \mu\text{eq-mg organic carbon}^{-1}$ . Johannessen [5] concluded that organic carbon was the most important weak acid/base system in acidic Norwegian waters because of the high organic carbon concentration relative to aluminum.

Glover and Webb [6] evaluated the acid/base chemistry of surface waters in the Tovdal region of southern Norway. The BNC of hydrogen ion was small compared to the BNC of weak acid systems. These investigators suggested that of the total weak acid BNC,  $40\text{--}60 \mu\text{eq-L}^{-1}$  could be attributed to dissolved aluminum and silicon, while  $20\text{--}50 \mu\text{eq-L}^{-1}$  could be attributed to natural organic acids. Solution titrations were characterized as having a major proton dissociation constant ( $K_a$ ) of  $10^{-6}$  to  $5 \times 10^{-7}$ , in addition to some less well defined ionization at higher pH values.

In a comparable study Henriksen and Seip [7] evaluated the strong and weak acid content of surface waters in southern Norway and southwestern Scotland. In addition to a titrimetric analysis, the aluminum, dissolved silica and TOC content of water samples were determined. Weak acid concentrations, determined by a Gran [8] calculation, were evaluated by multiple regression analysis. Most of the variance in the weak acid concentration could be explained by the aluminum and TOC content of the waters. Thus it was concluded that the weak acid content of acidified lakes in southern Norway and Scotland was largely a mixture of aluminum and natural organic acids.

Although some research on the weak acid/base content of dilute, acidified water systems has been done in Europe, there have been few, if any, studies in North America. The intent of this research was to quantify the weak acid/base chemistry of dilute acidified lake and stream systems in the Adirondack Mountain region of New York state.

## EXPERIMENTAL SITE AND METHODS

Water samples were collected over an annual cycle at three lakes, Big Moose Lake ( $74^{\circ}55'$  W,  $43^{\circ}30'$  N), North Lake ( $74^{\circ}51'$  W,  $43^{\circ}43'$  N) and Little Moose Lake ( $74^{\circ}55'$  W,  $43^{\circ}42'$  N) and eight tributaries, a total of 24 sites. Samples were collected approximately every three weeks in the spring, summer and autumn, and every four weeks in the winter; a total of 15 sampling dates.

pH was determined potentiometrically with a glass electrode. Free fluoride was measured potentiometrically with a fluoride ion selective electrode. Sulfate was measured by the turbidimetric method [9]. TOC was determined by oxidation, followed by infrared detection of  $\text{CO}_2$ . Basic cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) were determined by atomic absorption spectrophotometry (AAS). Lanthanum was added

**Table I.** Equilibrium Relationships Used in This Study

<i>Equation</i>	<i>Equilibrium Constant</i>	<i>Reference</i>
<b>Hydroxide Ligands</b>		
$\text{Al}^{3+} + \text{H}_2\text{O} = \text{Al}(\text{OH})^{2+} + \text{H}^+$	$1.03 \times 10^{-5}$	13
$\text{Al}^{3+} + 2\text{H}_2\text{O} = \text{Al}(\text{OH})_2^+ + 2\text{H}^+$	$7.36 \times 10^{-11}$	13
$\text{Al}^{3+} + 4\text{H}_2\text{O} = \text{Al}(\text{OH})_4^- + 4\text{H}^+$	$6.93 \times 10^{-23}$	13
<b>Fluoride Ligands</b>		
$\text{Al}^{3+} + \text{F}^- = \text{AlF}^{2+}$	$1.05 \times 10^7$	14
$\text{Al}^{3+} + 2\text{F}^- = \text{AlF}_2^+$	$5.77 \times 10^{12}$	14
$\text{Al}^{3+} + 3\text{F}^- = \text{AlF}_3$	$1.07 \times 10^{17}$	14
$\text{Al}^{3+} + 4\text{F}^- = \text{AlF}_4^-$	$5.37 \times 10^{19}$	14
$\text{Al}^{3+} + 5\text{F}^- = \text{AlF}_5^{2-}$	$8.33 \times 10^{20}$	14
$\text{Al}^{3+} + 6\text{F}^- = \text{AlF}_6^{3-}$	$7.49 \times 10^{20}$	14
<b>Sulfate Ligands</b>		
$\text{Al}^{3+} + \text{SO}_4^{2-} = \text{AlSO}_4^+$	$1.63 \times 10^3$	14
$\text{Al}^{3+} + 2\text{SO}_4^{2-} = \text{Al}(\text{SO}_4)_2^-$	$1.29 \times 10^5$	14
<b>Inorganic Carbon Equilibria</b>		
$\text{CO}_{2(g)} + \text{H}_2\text{O} = \text{H}_2\text{CO}_3^*$	$3.39 \times 10^{-2}$	15
$\text{H}_2\text{CO}_3^* = \text{H}^+ + \text{HCO}_3^-$	$4.47 \times 10^{-7}$	15
$\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$	$4.68 \times 10^{-11}$	15

to samples to minimize potential interference by dissolved silica, aluminum, sulfate or orthophosphate in the determination of calcium and magnesium [10]. Specific conductance was determined using a conductivity bridge [9].

Monomeric aluminum was measured using the colorimetric, ferron-ortho-phenanthroline method as suggested by Smith [11]. Organic monomeric aluminum (Org-Al) was separated using an ion exchange chromatography technique and measured as monomeric aluminum [12]. Details of the ion exchange chromatography technique are summarized elsewhere [12]. Inorganic monomeric aluminum (Inorg-Al) was calculated as the difference between monomeric aluminum and organic monomeric aluminum.

Water quality data were examined with respect to chemical equilibria. The thermodynamic relationships used in this study are summarized in Table I [13–15]. The equations used for calculating various aluminum species are summarized elsewhere [2,12]. Activity corrections were made using the Debye–Huckel relationship [15].

### Titrimetric Determinations

The ANC of water samples was determined by titration with strong acid. To estimate the ANC of a water sample it is necessary to determine analytically the equivalence point of the titration. This determination can be accomplished by a

Gran plot analysis. The Gran titrimetric technique was developed by Gran [8] and has been discussed by many authors [16–19]. The ANC of a monoprotic weak acid/base system can be described as follows:

$$\text{ANC} = [\text{A}^-] + [\text{OH}^-] - [\text{H}^+] \quad (1)$$

where     $\text{ANC}$  = sample acid neutralizing capacity ( $\text{eq-L}^{-1}$ )  
            $[\text{A}^-]$  = weak base content of the water sample ( $\text{mol-L}^{-1}$ )

As the titration proceeds, the hydrogen ion in the titrant is added to solution and the weak base becomes protonated (HA). Eventually the weak base and hydroxide ion content of the solution will decrease and the hydrogen ion content will increase until the ANC is zero ( $[\text{H}^+] = [\text{A}^-] + [\text{OH}^-]$ ). This occurs at the equivalence point and the volume of titrant required to reach this point in the titration is termed the equivalent volume of titrant ( $V_e$ ). With the equivalent volume of titrant it is possible to calculate the ANC of a sample:

$$\text{ANC} = V_e \times \bar{C}_a \times V_o^{-1} \quad (2)$$

where     $V_e$  = volume of strong acid required to reach the equivalence point of the titration (L)  
            $\bar{C}_a$  = normality of the titrant ( $\text{eq-L}^{-1}$ )  
            $V_o$  = original sample volume (L)

In addition, any point on the titration curve may be defined relative to the equivalence point:

$$\text{ANC}_v = (V_e - V) \times \bar{C}_a \times (V_o + V)^{-1} \quad (3)$$

where     $\text{ANC}_v$  = ANC of any point on the titration curve ( $\text{eq-L}^{-1}$ )  
            $V$  = volume of titrant added (L)

When the volume of titrant ( $V$ ) exceeds the equivalent volume ( $V_e$ ), the  $\text{ANC}_v$  becomes negative and the following approximation is valid:

$$[\text{H}^+] \gg [\text{A}^-] + [\text{OH}^-] \quad (4)$$

$$\text{ANC} \approx -[\text{H}^+] \quad (5)$$

This approximation for ANC (Equation 5) may be substituted into Equation 3 and rearranged to obtain

$$(V_o + V)([\text{H}^+]) \approx (V - V_e) \bar{C}_a \quad (6)$$

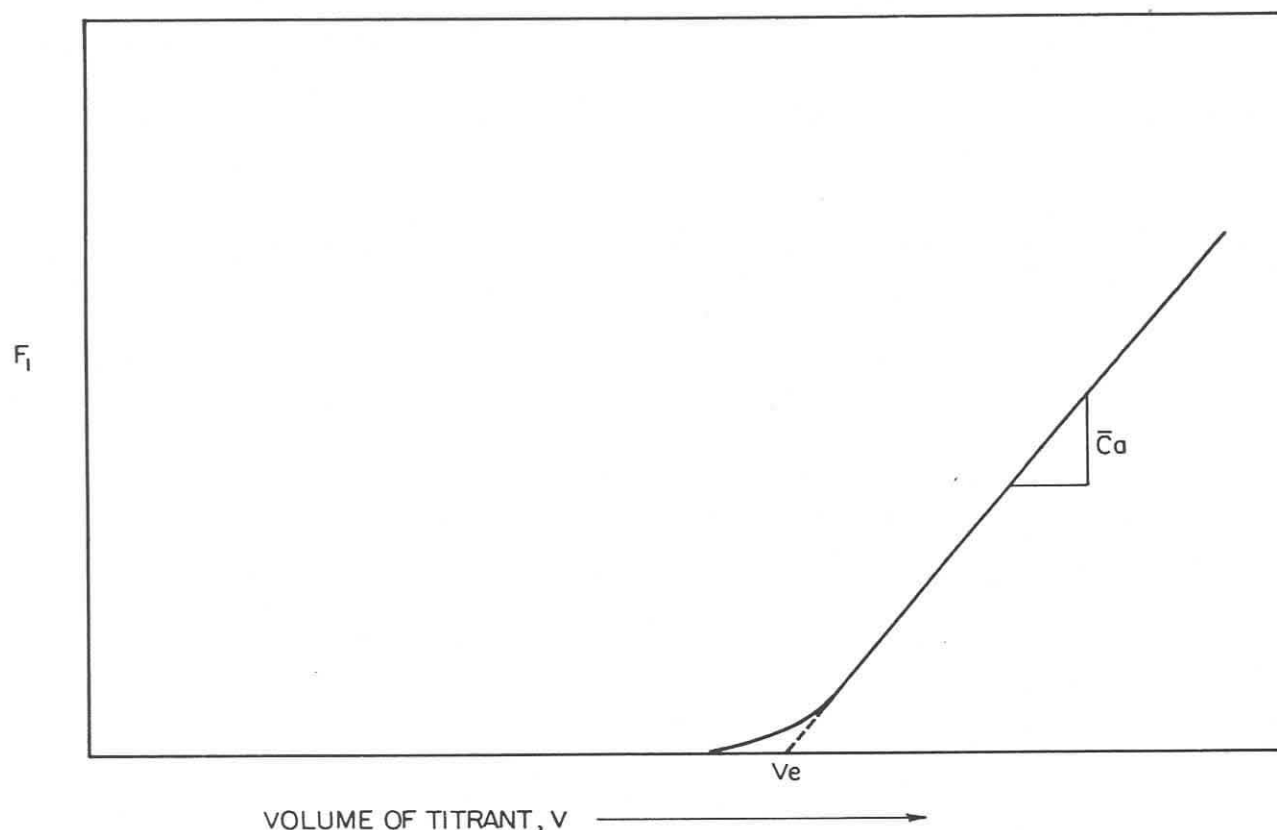
and finally

$$F_1 = (V_0 + V) 10^{-\text{pH}} \approx (V - V_e) \bar{C}_a \quad (7)$$

where  $F_1$  = ANC Gran function

If  $F_1$  is plotted as a function of the titrant volume (Figure 1), the linear portion of the plot can be extrapolated to  $F_1 = 0$ , to obtain the equivalent volume ( $V_e$ ). In addition, the slope of this plot should equal the normality of the titrant ( $\bar{C}_a$ ).

Two potential sources of error are associated with a Gran analysis. The first is termed the weak base error. If in the pH range of linear extrapolation, there is a significant concentration of weak base ( $A^-$ ), then the approximation made in Equations 4 and 5 is not valid and an error will result in the ANC determination. The titration of weak base will result in a low value of  $F_1$  and a decrease in the slope of the linear portion of the Gran plot. In turn, the linear extrapolation will produce a lower value of the equivalent volume ( $V_e$ ) and this will result in an underestimate of the measurement of ANC.



**Figure 1.** Schematic illustration of a Gran plot. The linear portion of the curve is extrapolated to determine the equivalent volume ( $V_e$ ). The slope of the plot corresponds to the normality of the titrant.

To illustrate the magnitude of the weak base error, consider a sample volume containing a monoprotic weak acid/base system that has a  $pK_a$  value of 5 and a total concentration (CT) of  $2 \times 10^{-5} \text{ mol-L}^{-1}$ :

$$CT = [HA] + [A^-] \quad (8)$$

This sample is titrated with 0.1 *N* HCl. To evaluate the weak base error of this model system,  $F_1$  was evaluated as a function of titrant volume. The linear extrapolation of  $F_1$  was made over three separate pH ranges and apparent values of  $V_e$  and ANC were calculated (Table II). The analysis was done at pH intervals of 0.1 pH unit (11 points), and the extrapolation to  $F_1 = 0$  was done by a linear regression analysis. It is apparent that to minimize the weak base error the pH range of linear extrapolation must be considerably below the  $pK_a$  value of the weak acid/base systems present in the sample. It is noteworthy that high correlation coefficient ( $r^2$ ) values were observed in the linear regression of the Gran function even though there was significant weak base error. It appears that the slope of the Gran plot is a better indicator of potential weak base error than the correlation coefficient of the linear extrapolation. To minimize weak base error in solutions it is best to evaluate the Gran function over a pH range as far below solution proton dissociation constants as possible.

While titrating samples to as low a pH value as possible will minimize the weak base error, it will introduce a pH reading error. This is simply due to the fact that hydrogen ion activity is greater at lower pH values. A given error in a pH reading is magnified at low pH values because the linear extrapolation of the Gran plot is made over a greater range and therefore will result in a greater error in the ANC determination.

In this study ANC was measured by incremental strong acid (0.1 *N* HCl) titrations, in equilibrium with atmospheric carbon dioxide, to pH 3.0–3.2. The titration curves were analyzed as Gran plots and the ANC was determined. Of the weak acid/base systems present in the water samples, natural organic matter had proton dissociation constant ( $pK_a$ ) values between 4.0 and 5.0, while aluminum

**Table II.** Effect of the pH Range of Linear Extrapolation of the Gran Function on Acid Neutralizing Capacity Measurement for a Monoprotic Weak Acid/Base System with  $CT = [HA] + [A^-] = 2.0 \times 10^{-5}$  and  $pK_a = 5$ . The Titrant Normality is 0.1 eq-L<sup>-1</sup>.

	<i>pH Range of Linear Extrapolation</i>		
	4.0 $\approx$ 5.0	3.5 $\approx$ 4.5	3.0 $\approx$ 4.0
$r^2$	0.9986	0.9999	1.000
Gran Plot Slope (eq-L <sup>-1</sup> )	0.0921	0.0987	0.0998
Measured $[A^-]$ (eq-L <sup>-1</sup> )	11.9	16.2	18.6
Measured $[A^-]$ /Theoretical $[A^-]$	0.60	0.81	0.93



has a first hydrolysis constant ( $p^*K_{s1}$ ) of about 5.0. It is evident that there was some weak base error and pH reading error in these titrations. However the pH range of linear extrapolation, of the Gran plots, was chosen to minimize both sources of error.

### ANC Fractionation

The second set of ANC measurements made in this study involved the fractionation of non-inorganic carbon ANC into aluminum and natural organic carbon components. In this analysis three separate sets of titrations were performed on each sample. A 100-mL sample was acidified to pH 3 with 0.1 *N* HCl and purged with nitrogen for at least 20 min to remove any inorganic carbon. To the sample 100  $\mu$ L of 1 *N* Tris buffer [tris(hydroxymethyl) aminomethane] was added. The Tris buffer served to raise the pH so that strong acid titrations could be made and to provide some buffering in the pH 5–7 range so that titration curves could be examined in detail. Samples were titrated with 0.1 *N* HCl using calibrated micropipets (20, 50 and 100  $\mu$ L) to a pH value of approximately 3.0. This procedure was done on the original water sample, an aliquot of water sample that was passed through an ion exchange chromatography column to remove inorganic monomeric aluminum (aluminum desalted) and on a distilled water blank. The ion exchange chromatography procedure was the same as that used to separate inorganic and organic aluminum forms.

An example of a fractionated titration curve resulting from this procedure is illustrated in Figure 2. The equivalence points of these titration curves were evaluated by a Gran analysis [8]. It is evident that there are three distinct titration curves. The difference between the total titration curve and the aluminum desalted curve was considered to be an estimate of the aluminum ANC. The difference between the aluminum desalted curve and the distilled water background curve was an estimate of the ANC due to natural organic matter.

With titration curves for each fraction of aqueous ANC, it was possible to use the concept of weak base error to calculate the proton dissociation constant ( $pK_a$ ) and the total concentration of proton dissociable/associable material (CT). This calculation was made by utilizing a Gran function, corrected for the presence of weak base. The Gran function corrected for the presence of a monoprotic weak base, with Tris buffer added may be written as follows:

$$F_1^c = (V_0 - V)([H^+] - [OH^-] - [A^-] - [Tris^-]) = \bar{C}_a (V_e - V) \quad (9)$$

where  $F_1^c$  = weak base corrected Gran function  
 $Tris^-$  = basic form of Tris ( $\text{mol-L}^{-1}$ )

The weak bases ( $A^-$ ,  $Tris^-$ ) may be calculated from equilibrium and mass balance relationships:

$$[A^-] = \frac{CT_{A^-} \times K_{A^-}}{K_{A^-} + \{H^+\}/\gamma_{A^-}} \quad (10)$$

$$[Tris^-] = \frac{CT_{Tris} \times K_{Tris}}{K_{Tris} + \{H^+\}/\gamma_{Tris}} \quad (11)$$

where  $\gamma$  = activity coefficient for an aqueous form of interest

$K$  = proton dissociation constant of the acid/base form of interest, e.g.,

$$K_{A^-} = \frac{\{H^+\}\{A^-\}}{\{HA\}} \quad (12)$$

The subscript  $A^-$  represents either aluminum or organic matter depending on what fraction is being analyzed. Substituting Equations 10 and 11 into Equation 9, and converting concentrations to activity, the following working Gran relationship is obtained.

$$F_1^c = [(V_0 + V)\{H^+\}/\gamma_{H^+}] + [\{OH^-\}/\gamma_{OH^-}] - \left[ \frac{(CT_{A^-} \times K_{A^-})}{(K_{A^-} + \{H^+\}/\gamma_{A^-})} \right] - \left[ \frac{(CT_{Tris} \times K_{Tris})}{(K_{Tris} + \{H^+\}/\gamma_{Tris})} \right] \quad (13)$$

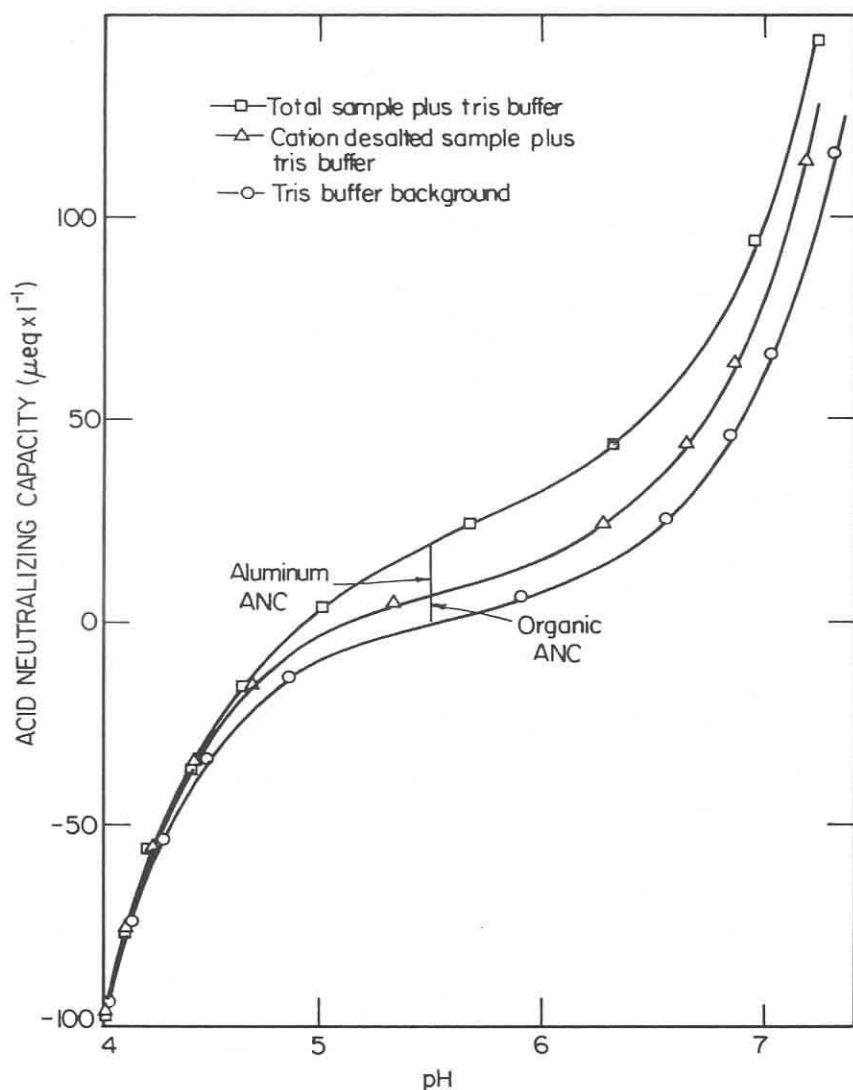
The value of  $K_{Tris}$  is reported to be  $8.32 \times 10^9$  at 25C [19]; this was verified titrimetrically. The titration curve of the aluminum desalted sample was initially analyzed in conjunction with Equation 12 to compute  $K_{A^-}$  and  $CT_{A^-}$ . This analysis required an initial guess of  $CT_{A^-}$  and  $K_{A^-}$ , and the weak base corrected Gran function ( $F_1^c$ ) was calculated.  $pK_{A^-}$  and then  $CT_{A^-}$  were incremented until a maximum correlation coefficient ( $r^2$ ) was observed. The  $pK_{A^-}$  and  $CT_{A^-}$  values at the maximum correlation coefficient of the weak base corrected Gran function represented the best fit of the titration data to a monoprotic weak acid/base system.

The values of  $pK_{A^-}$  and  $CT_{A^-}$  obtained from the data analysis of the aluminum desalted sample titration were designated as  $pK_{org}$  and  $CT_{org}$  respectively and used in the modified Gran function:

$$F_1^c = [(V_0 + V)\{H^+\}/\gamma_{H^+}] + [\{OH^-\}/\gamma_{OH^-}] - \left[ \frac{(CT_{A^-} \times K_{A^-})}{(K_{A^-} + \{H^+\}/\gamma_{A^-})} \right] - \left[ \frac{(CT_{Tris} \times K_{Tris})}{(K_{Tris} + \{H^+\}/\gamma_{Tris})} \right] - \left[ \frac{(CT_{org} \times K_{org})}{(K_{org} + \{H^+\}/\gamma_{org})} \right] \quad (14)$$

The iterative procedure was then applied using Equation 14 to the total sample. The values  $pK_{A^-}$  and  $CT_{A^-}$  obtained from this analysis were assumed to be due to inorganic aluminum. It should be noted that this analysis is not subject to the weak base error previously discussed.

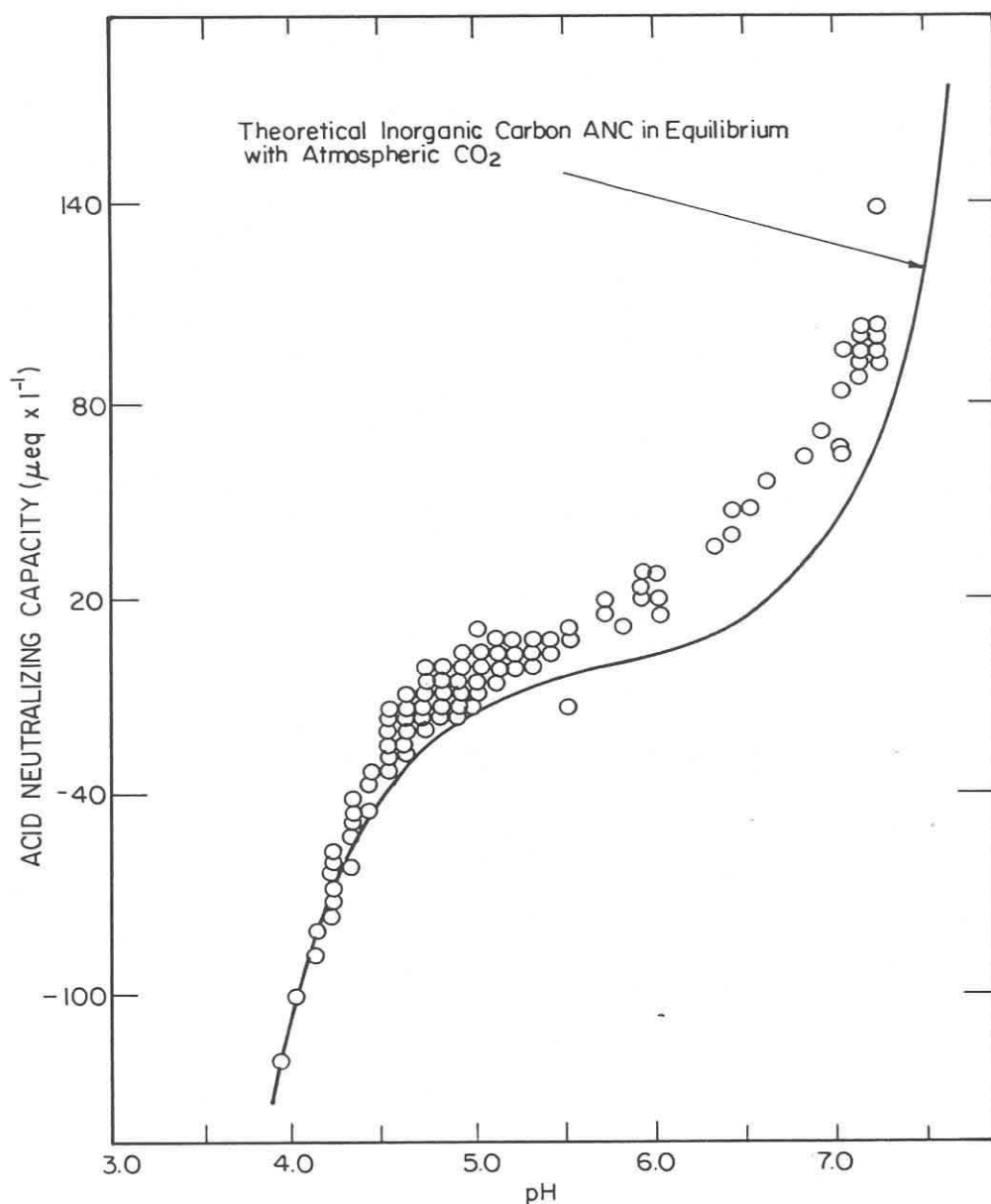




**Figure 2.** A fractionated titration curve. The difference in ANC between the total sample and the aluminum desalted sample was considered to be the aluminum ANC. The difference between the aluminum desalted sample and the Tris background curve was considered to be the organic carbon ANC.

## RESULTS

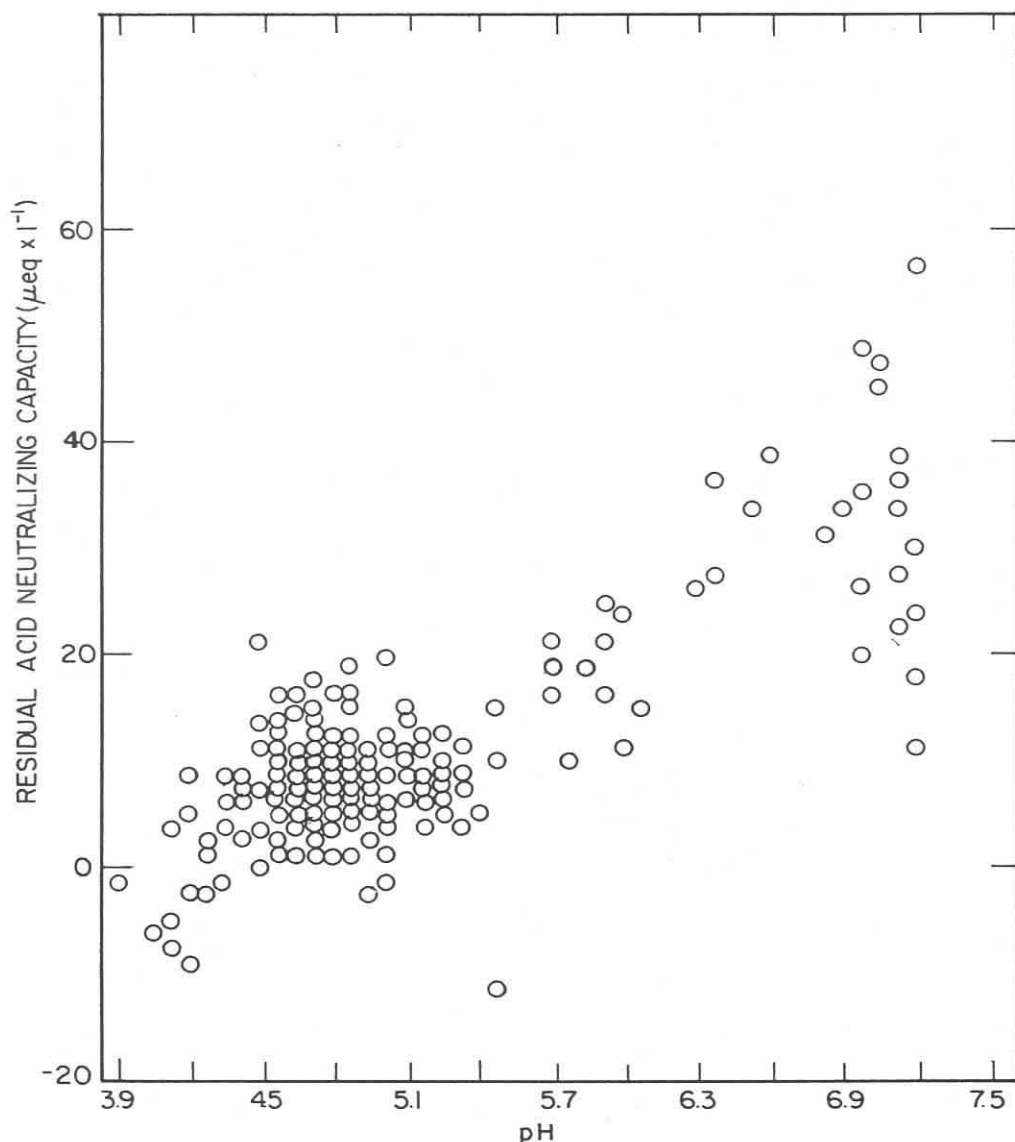
ANC and pH values in equilibrium with atmospheric  $\text{CO}_2$  obtained from this study are represented in Figure 3. Superimposed on this plot is a theoretical titration curve of water in equilibrium with atmospheric  $\text{CO}_2$ . It is apparent that, in general, Adirondack waters had a greater ANC than expected based on equilibrium with atmospheric  $\text{CO}_2$ . The difference between the measured ANC, and theoretical ANC in equilibrium with atmospheric  $\text{CO}_2$ , might be considered to be the residual ANC (res. ANC), which would represent non-inorganic carbon bases (e.g., aluminum or natural organic matter). A plot of the residual ANC as a function of pH is presented in Figure 4. The mean residual ANC value was  $9.7 \mu\text{eq-L}^{-1}$ . Residual ANC was strongly correlated with pH (Figure 3), which might be expected because weak acid/base systems would be deprotonated to a greater degree at higher pH values. A multiple regression analysis of the TOC, aluminum and dissolved silica suggested that TOC, inorganic aluminum and dissolved silica could only slightly explain the observed variance (Figure 4). However the results of this analysis



**Figure 3.** ANC values as a function of pH for samples collected in this study. Superimposed on this plot is the theoretical inorganic carbon ANC in equilibrium with atmospheric carbon dioxide ( $P_{\text{CO}_2} = 10^{-3.5}$  atm). The difference between the actual ANC and the theoretical inorganic carbon ANC at a given pH is considered to be the residual ANC, which may be attributed to aluminum or natural organic carbon.

were not totally unexpected. Only a fraction of the aluminum and organic carbon in solution participates in proton consumption reactions, and this fraction is a strong function of solution pH. So it is not unreasonable to suggest that multiple regression analysis would be a poor means of quantifying residual ANC.

A more reasonable approach would be to examine the chemical equilibrium of the solution with respect to proton donor/acceptor reactions. The monoprotic



**Figure 4.** Residual ANC as a function of pH for samples collected in this study. A multiple regression analysis yielded the following empirical relationships: Res. ANC =  $-5.06 \times 10^{-5} + 1.21 \times 10^{-5} (\text{pH})$ ,  $r^2 = 0.55$ ; Res. ANC =  $-5.52 \times 10^{-5} + 1.21 \times 10^{-5} (\text{pH}) + 7.77 \times 10^{-7} (\text{TOC})$ ;  $r^2 = 0.57$ ; Res. ANC =  $-7.02 \times 10^{-5} + 1.44 \times 10^{-5} (\text{pH}) + 8.68 \times 10^{-7} (\text{TOC}) + 1.71 \times 10^{-5} (\text{Inorg-Al})$ ,  $r^2 = 0.60$ .

weak acid/base systems chosen for this analysis are a simplified representation of proton equilibria. Aluminum is a hydrolyzing metal with an insoluble phase [13]. Natural organic acids generally exhibit a “smeared” titration curve, which has been attributed to several functional groups [21] or electrostatic interactions between the same type of functional groups [22]. While the monoprotic weak acid/base analysis presented here is a simplification of the actual system, interesting information with regard to the nature of acid/base systems in Adirondack waters may still be obtained.

The results of the organic carbon ANC analysis are summarized in Table

**Table III.** Summary of pKorg Values Observed in this Study

	<i>Acidic Streams</i>	<i>Acidic Lakes</i>	<i>Nonacidic Lake</i>	<i>Total</i>
Number of Observations	25	12	5	42
Mean Value	4.44	4.48	4.06 <sup>a</sup>	4.41
95% Confidence Interval	±0.41	±0.46	±1.05	±0.55

<sup>a</sup> This value is statistically different ( $P < 0.1$ ) from acidified lake pKorg values.

III. Proton dissociation constants were comparable with values obtained from other investigators [21]. Observed pKorg values for acidified streams were similar in magnitude to those of acidified lakes. Limited observations were also made for a neutral-pH lake (Little Moose Lake, pH >7); proton dissociation constant values were greater (pKa values were lower) than those for acidified lakes ( $P > 0.1$ , *t* test). In acidic lakes and streams, aluminum was to a large extent complexed with natural organic matter. The increase in observed pKorg values in acidified waters may be due to the association of hydrolyzable aluminum with natural organic matter.

Empirical relationships were observed between TOC and CTorg (Table IV). Trends for total and stream data sets were statistically significant, while no statistically significant trend was observed for lake systems. The poor correlation between CTorg and TOC and lake systems may be due to the presence of autochthonous organic carbon (e.g., algae) that might not significantly participate in proton dissociation reactions. It is interesting to compare the relationship between CTorg and TOC observed in this study with values reported by other investigators (Table V) [5,7,23]. It is apparent that the value presented by Schnitzer [23] for a "model" fulvic acid is considerably greater than values observed for acidified waters. It is

**Table IV.** Comparison of CTorg–TOC and CT<sub>Al</sub>–Inorg–Al Empirical Equations for Total, Lake and Stream Data Sets (CT is expressed in mols-L<sup>-1</sup>, TOC is expressed as mg-L<sup>-1</sup> of C and Inorg-Al is expressed as mg-L<sup>-1</sup> of Al)

<i>Empirical Equation</i>	<i>n</i>	<i>Standard Error</i>		<i>r</i> <sup>2</sup>	<i>Significance Level, P</i>
		<i>Slope</i>	<i>Intercept</i>		
Total Data	42				
CTorg = 7.54 + 2.65(TOC)		0.34	2.21	0.60	<0.0001
CT <sub>Al</sub> = 13.7 + 43.0(Inorg-Al)		10.5	2.31	0.30	<0.0002
Lakes Data	17				
CTorg = 14.1 + 0.42(TOC)		1.04	4.18	0.01	<0.69
CT <sub>Al</sub> = 8.0 + 52.9(Inorg-Al)		14.0	2.26	0.48	<0.002
Streams Data	25				
CTorg = 9.40 + 2.57(TOC)		0.42	3.28	0.61	<0.0001
CT <sub>Al</sub> = 18.8 + 33.3(Inorg-Al)		13.2	3.21	0.22	<0.02

**Table V.** A Comparison of Total, Organic Carbon Proton Dissociation Sites Observed in this Study with Values Reported by Other Investigators

<i>Total, Organic Carbon Proton Dissociation/Association Sites (<math>\mu\text{mols-mg Org-C}^{-1}</math>)</i>	<i>Reference</i>
20	23
5.5	7
7.5	5
2.6	This study

also noteworthy that the value of total, organic acid proton dissociation/association sites per milligram of organic carbon observed in this study is less than values observed in studies of acidic lakes in Norway.

Titration data would suggest (Figure 2) that the aluminum system was dissociating at a higher pH value than the organic carbon system. The mean  $\text{pK}_{\text{Al}}$  value of the inorganic aluminum system (the total less aluminum desalted fraction) was 5.55 [ $\text{P}(4.82 \leq \mu \leq 6.28) = 0.05$ ]. This agreed well with  $\text{AlCl}_3$  solutions, which were also titrated and analyzed as a monoprotic system ( $\text{pK}_{\text{Al}} = 5.45$ ). Empirical relationships were observed between  $\text{CT}_{\text{Al}}$  and the inorganic monomeric aluminum content ( $\text{Inorg-Al}$ ) of water samples in total, lakes and streams data sets (Table IV).

While fitting aluminum titrations to a monoprotic dissociation model may yield interesting empirical observations, it is not a realistic model due to the fact that aluminum is a hydrolyzing metal. Aluminum chemistry was also evaluated using water quality observations from lake and stream systems. Aquo aluminum levels were calculated using inorganic monomeric aluminum, pH, sulfate and free fluoride values as well as pertinent equilibrium constants (Table I). Aquo aluminum levels closely followed an aluminum trihydroxide solubility model. Values of the logarithm of the ion activity quotient (Equation 15) for an aluminum trihydroxide model are summarized in Table VI.

$$Q_p = \frac{\{\text{Al}^{3+}\}}{\{\text{H}^+\}^3} \quad (15)$$

where  $Q_p$  = ion activity quotient  
 $\{\text{Al}^{3+}\}$  = aquo aluminum activity

$Q_p$  values were very similar for lake and stream systems. These  $Q_p$  values are close in value to the equilibrium constant reported by May et al. [13] for a natural gibbsite ( $\log^* K_{\text{so}} = 8.77$ ). A plot of  $\text{pAl}^{3+}$  as a function of pH should yield a linear relationship with a slope of 3 for an aluminum trihydroxide phase. A linear regression of  $\text{pAl}^{3+}$  as a function of pH for data obtained in this study yields slope values slightly less than three (Table VII). A comparison of the  $\text{pAl}^{3+}$ -

**Table VI.** Summary of Ion Activity Quotient Values ( $Q_p$ ) for an Aluminum Trihydroxide Model ( $3\text{pH}-\text{pAl}^{3+}$ )

	<i>Stream Data</i>	<i>Lake Data</i>	<i>Total Data</i>
Number of Observations	116	205	321
Mean Value	8.44	8.52	8.49
95% Confidence Interval	$\pm 1.31$	$\pm 0.51$	$\pm 0.88$

pH relationships for lake and stream data sets shows a considerable difference between the two systems. The  $\text{pAl}^{3+}$ -pH slope for lake data (2.64) was considerably greater than that observed for streams. It is reasonable that lake data would more closely resemble an ideal aluminum trihydroxide system than stream data. Streams are more subject to dramatic changes in water quality than are lakes. Under high-flow, low-pH conditions (spring snowmelt and rainfall events), the dissolution rate of  $\text{Al}(\text{OH})_3$  may not be able to maintain a constant aluminum solubility ( $Q_p$ ). If lake surface water samples during spring snowmelt, which were highly undersaturated with respect to  $\text{Al}(\text{OH})_3$ , are excluded from this analysis, lakewater data very closely resemble  $\text{Al}(\text{OH})_3$  equilibria (Table VII).

An empirical relationship was observed between the organic monomeric fraction of aluminum (Org-Al) and TOC (Table VII). The organic monomeric aluminum-TOC relationships were similar for both lake and stream systems. The slopes of these two empirical relationships were almost identical for both data sets. However, the ordinate intercept of the lakes data set is less than that of the streams data set. This implies that lakewater contains more nonaluminum-complexing or-

**Table VII.** Comparison of  $\text{pAl}^{3+}$ -pH and Org-Al-TOC Empirical Equations for Total, Lake and Stream Data Sets (Org-Al is expressed in  $\text{mg-L}^{-1}$  of Al, TOC is expressed in  $\text{mg-L}^{-1}$  of C)

<i>Empirical Equation</i>	<i>n</i>	<i>Standard Error</i>		<i>r</i> <sup>2</sup>	<i>Significance Level, P</i>
		<i>Slope</i>	<i>Intercept</i>		
<b>Total Data</b>					
pAl <sup>3+</sup> = −6.55 + 2.55(pH)	321	0.042	0.229	0.93	<0.0001
Org-Al = −0.088 + 0.046(TOC)	322	0.0015	0.0086	0.76	<0.0001
<b>Lakes Data</b>					
pAl <sup>3+</sup> = −6.63 + 2.64(pH)	205	0.042	0.209	0.95	<0.0001
pAl <sup>3+</sup> = −7.32 + 2.76(pH) <sup>a</sup>	191	0.027	0.135	0.98	<0.0001
Org-Al = −0.084 + 0.046(TOC)	205	0.0020	0.0103	0.70	<0.0001
<b>Streams Data</b>					
pAl <sup>3+</sup> = −5.50 + 2.40(pH)	116	0.088	0.442	0.88	<0.0001
Org-Al = −0.046 + 0.046(TOC)	117	0.0022	0.0154	0.77	<0.0001

<sup>a</sup> This represents lakewater data with 14 lake meltwater samples excluded.



ganic carbon than does stream water, which could be attributed to autochthonous organic carbon.

## DISCUSSION OF RESULTS

The acid/base chemistry of dilute acidified surface waters may be best summarized by the system's buffer intensity ( $\beta$ ). Buffer intensity is a measure of the system's ability to withstand changes in pH:

$$\beta = \frac{dC_B}{dpH} = - \frac{dC_A}{dpH} \quad (16)$$

where  $\beta$  = buffer intensity  
 $dC_B, dC_A$  = quantity of strong base or strong acid ( $\text{mol-L}^{-1}$ ) required to produce an incremental change in pH of  $dpH$ .

Stumm and Morgan [15] and van Breemen and Wielemaker [24] provide excellent discussions on the thermodynamic nature of buffer intensity. The buffer intensity of four acid/base systems pertinent to dilute acidified waters [water ( $\text{H}^+$ ,  $\text{OH}^-$ ), inorganic carbon, aluminum and organic carbon] are:

$$\beta_{\text{H}_2\text{O}} = 2.303 ([\text{H}^+] + [\text{OH}^-]) \quad (17)$$

$$\beta_{\text{PCO}_2} = 2.303 ([\text{HCO}_3^-] + 4 [\text{CO}_3^{2-}]) \quad (18)$$

$$\beta_{\text{Al}} = 2.303 (9[\text{Al}^{3+}] + 9[\text{Al-F}] + 9[\text{Al-SO}_4] + 4[\text{Al(OH)}^{2+}] + [\text{Al(OH)}_2^+] + [\text{Al(OH)}_4^-]) \quad (19)$$

$$\beta_{\text{RCOOH}} = 2.303 ([\text{RCOOH}] + [\text{RCOO}^-]) \quad (20)$$

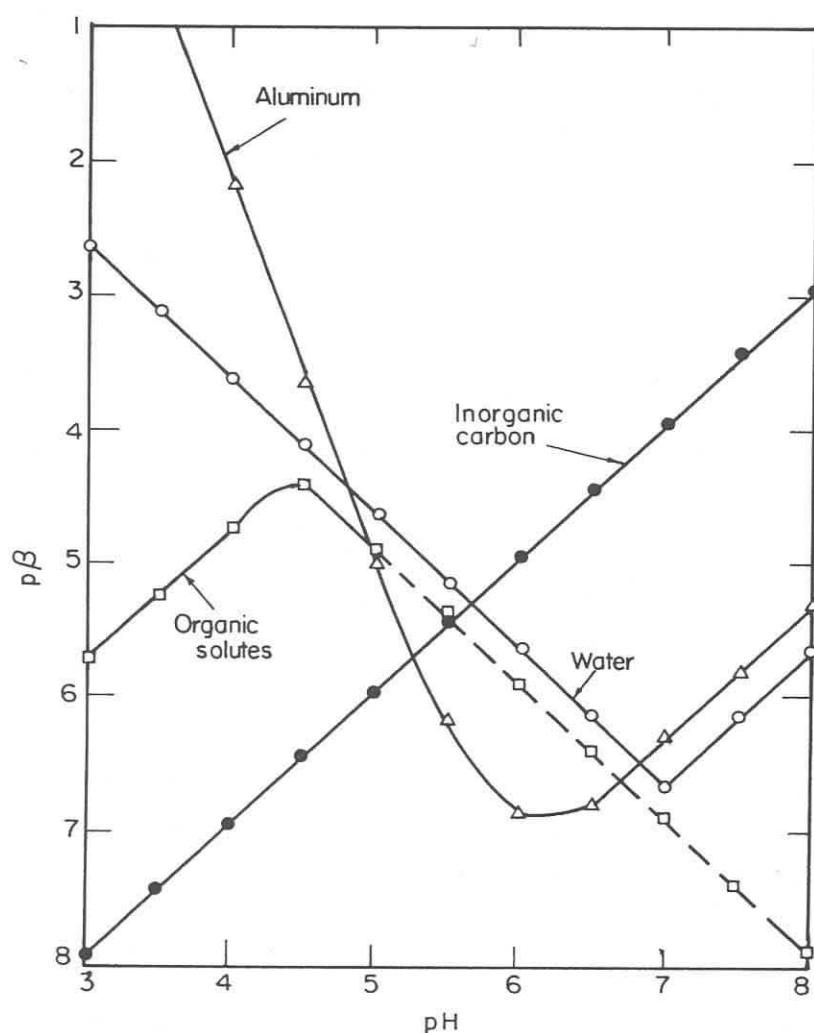
where  $[\text{Al-F}], [\text{Al-SO}_4]$  = sum of the aluminum fluoride and aluminum sulfate complexes, respectively ( $\text{mol-L}^{-1}$ )  
 $[\text{RCOOH}], [\text{RCOO}^-]$  = protonated and unprotonated forms of natural organic carbon, respectively ( $\text{mol-L}^{-1}$ )

The development of these equations is summarized by van Breemen and Wielemaker [24]. To apply these buffer intensity relationships to Adirondack surface waters the following conditions were assumed:

1. The system was in equilibrium with atmospheric carbon dioxide ( $P_{\text{CO}_2} = 10^{-3.5} \text{ atm}$ ).
2. The system had a fluoride content of  $0.1 \text{ mg-L}^{-1}$  and a sulfate content of  $6.0 \text{ mg-L}^{-1}$ .
3. The system was in equilibrium with an aluminum trihydroxide phase with a solubility constant of  $*K_{\text{so}} = 10^{8.49} = [\text{Al}^{3+}]/[\text{H}^+]^3$ .
4. The system has an ionic strength of  $3 \times 10^{-4}$ .

5. The system has a TOC content of  $5 \text{ mg-L}^{-1}$ , which corresponds to  $CT_{\text{org}} = 2.0 \times 10^{-5} \text{ mol-L}^{-1}$ ; this organic acid system has a monoprotic proton dissociation constant of  $K_{\text{org}} = 10^{-4.4} = \{H^+\}\{RCOO^-\}/\{RCOOH\}$ .

The above conditions were considered to be representative of the mean water quality data observed in this study and therefore representative of acidic Adirondack waters. Appropriate thermodynamic relationships were applied to Equations 17–20 and individual buffer intensity values were computed for a range of pH values. A negative logarithm of the buffer intensity ( $p\beta$ ) diagram is presented in Figure 5. At low pH values ( $\text{pH} < 5$ ), the system is strongly buffered by the aluminum. As the pH increases, aluminum buffer intensity decreases dramatically. In the pH range 5–6 the buffer intensity reaches a minimum. The buffer intensity of water ( $[H^+]$ ) and organic solutes are significant in this pH range. As the solution pH value increases above 6 the inorganic carbon system becomes the predominant buffering system. These calculations were based on the assumption that the system was in equilibrium with atmospheric carbon dioxide ( $P_{\text{CO}_2} = 10^{-3.5} \text{ atm}$ ). As a result, the inorganic carbon buffering illustrated here would represent the maximum that could be observed. If the system was not in equilibrium with atmospheric



**Figure 5.** Buffer intensity diagram for dilute Adirondack water systems. Equilibrium with aluminum trihydroxide ( $pK_{\text{so}} = 8.49$ ), organic solutes ( $CT_{\text{org}} = 2 \times 10^{-5}$ ,  $pK_{\text{org}} = 4.4$ ) and atmospheric carbon dioxide ( $P_{\text{CO}_2} = 10^{-3.5} \text{ atm}$ ) was assumed. The dashed line away from  $pK_{\text{org}}$  suggests that this model is not entirely representative of proton equilibria of natural organic carbon. Multiple functional group or electrostatic interaction models may more realistically simulate proton dissociation away from  $pK_{\text{org}}$ .

CO<sub>2</sub> the inorganic carbon buffering intensity would be smaller in magnitude. These calculations would suggest that the lower limit of pH values observed in acidic Adirondack waters was regulated by aluminum buffering.

### Significance and Application with Respect to Base Addition of Acidified Waters

Acidification of soft waters is a serious water quality problem. The results of this investigation may be applied to an understanding and possible solution of the problem of surface water acidification. One such solution might be the restoration of waters by base addition. The addition of base (CaO, Ca(OH)<sub>2</sub>, CaCO<sub>3</sub>) for water quality restoration has been practiced in regions experiencing acidification [24,25,26,27]. In order to achieve adequate neutralization it is necessary to consume all the system base neutralizing capacity (BNC), including aluminum and organic carbon BNC. To illustrate this consider a "typical" Adirondack lake (Table VIII) whose composition is based on mean observations obtained from this study. Utilizing this "typical" lake, estimates of the amount of base required to neutralize the system to pH 6.5 can be made, and are presented in Table IX. The calculations presented in Table IX were made by assuming:

1. The aqueous system was in equilibrium with atmospheric carbon dioxide ( $P_{\text{CO}_2} = 10^{-3.5}$  atm)
2. The  $5 \text{ mg C} \times \text{L}^{-1}$  corresponds to  $2 \times 10^{-5} \text{ mols} \times \text{L}^{-1}$  and the organic carbon system has a  $\text{pK}_a = 4.4$ .
3. Interactions with the sediment are negligible.

It is apparent (Table IX) that the aluminum and organic carbon systems represent a significant fraction ( $\approx 50\%$ ) of the aqueous BNC of Adirondack lake

**Table VIII.** Typical Adirondack Lakewater Composition (mg-L<sup>-1</sup> of Al, Except pH and TOC) with Respect to Parameters that Exert Base Neutralizing Capacity

<i>Parameter</i>	<i>Value</i>
pH	4.95
Inorganic Monomeric Aluminum	0.200
Aluminum Fluoride Forms	0.105
Aluminum Sulfate Forms	0.005
Aquoaluminum	0.040
Al(OH) <sup>2+</sup>	0.030
Al(OH) <sub>2</sub> <sup>+</sup>	0.020
TOC	5.0 <sup>a</sup>

<sup>a</sup> mg-L<sup>-1</sup> C.

**Table IX.** Amount of Base Required to Neutralize BNC Components of Typical Adirondack Lakewater to pH 6.5

<i>BNC Component</i>	<i>Base Required (<math>10^{-5}</math> eq-<math>L^{-1}</math>)</i>	<i>Percent of Total Base Required</i>
Hydrogen Ion	1.1	23
Inorganic Carbon	1.3	27
Aluminum	2.0	42
Organic Carbon	0.4	8
Total	4.8	100

systems. Therefore aluminum and organic carbon BNC should be considered when evaluating base addition requirements of acidified lakes.

It is noteworthy that Scheider et al. [26] suggest that sediments represent a significant base sink in acidic lakes. This study did not address this apparently important component of BNC.

## CONCLUSIONS

Based on this study it may be concluded that:

1. Natural organic carbon and inorganic aluminum are significant weak acid/base systems in dilute acidified waters of the Adirondack region of New York state.
2. Natural organic acids were fit to a monoprotic proton dissociation constant model ( $pK_a = 4.41$ ) and the total, organic carbon proton dissociation/association sites were observed to be empirically correlated to total organic carbon concentration.
3. Aquo aluminum levels appear to fit an aluminum trihydroxide solubility model.
4. Aluminum buffering appears to control the lower limit of pH value observed in Adirondack waters.

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